# Bose-Einstein condensation temperature of a gas of weakly dissociated diatomic molecules

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We consider the properties of a gas of bosonic diatomic molecules in the limit when few of the molecules are dissociated. Taking into account the effects of dissociation and scattering among molecules and atoms, we calculate the dispersion relation for a molecule, and the thermal depletion of the condensate. We calculate the dependence of the Bose-Einstein condensation temperature of a uniform gas on the atom-atom scattering length, and conclude that, for a broad Feshbach resonance, the condensation temperature increases as the molecular state becomes less strongly bound, thereby giving rise to a maximum in the transition temperature in the BEC-BCS crossover. We also argue on general grounds that, for a gas in a harmonic trap and for a narrow Feshbach resonance, the condensation temperature will decrease with increasing scattering length.

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## I. INTRODUCTION

The crossover between BCS pairing of two species of fermion and Bose-Einstein condensation of a diatomic molecules with changing atom-atom scattering length has been studied by many authors, beginning with the works of Eagles [1], Leggett [2] and Nozières and Schmitt-Rink [3]. One of the surprising results of the calculations of Ref. [3] and also found in Refs. [4, 5] is that, in the crossover region, the transition temperature has a maximum as the strength of the atom-atom interaction is varied. However, it is unclear whether the maximum is real, or merely an unphysical artifact of either the assumptions made in the model or the numerical procedures. The early calculations only accounted for quadratic fluctuations around the mean-field solution and it was generally expected that the fluctuation induced peak was an artifact of the gaussian approximation. This view was furthermore supported by a self-consistent field theoretical calculation in Ref. [6] where $T_{\rm c}$ was found to be a monotonic function of the dimensionless coupling constant. However, the most recent self-consistent calculations of $T_{\rm c}$ [7] do indicate the presence of a peak in $T_{\rm c}$. Most calculations for broad resonances for a uniform gas give a peak in $T_{\rm c}$ for both one-channel and two-channel models for the interaction, and for a variety of approximations for the atom propagators, which are in some cases replaced by either bare propagators, or by dressed propagators [8, 9, 10]. In calculations that use a combination of bare and dressed propagators, $T_{\rm c}$ initially decreases coming from the far BEC limit before turning around to give a local maximum near resonance [11]. In calculations for a harmonically trapped gas in the local density approximation, the peak vanishes for both one-channel and two-channel models for the interaction, and for a variety of approximations for the atom propagators [12]. The peak vanishes in calculations for sufficiently narrow resonances. A summary of the present situation is that microscopic calculations point to there being a maximum in $T_{\rm c}$ for broad resonances for the uniform gas, but not for harmonically trapped gases or sufficiently narrow resonances.

The purpose of this paper is to study the properties of a weakly dissociated gas of diatomic molecules composed of fermionic atoms with a view to determining whether or not the transition temperature $T_{\rm c}$ to a paired state should exhibit a maximum in the BEC-BCS crossover. We shall consider the molecule effective mass and the reduction of the density of molecules due to dissociation, as well as the interaction between molecules. As a consequence of critical fluctuations, molecule-molecule interactions lead to an increase in $T_{\rm c}$ away from the BEC limit and this effect dominates the decreases in $T_{\rm c}$ we find due to changes in the effective mass and the number of molecules. For a trapped gas, we shall argue that $T_{\rm c}$ should decrease away from the BEC limit due to the reduction of the central density in the trap as a consequence of the increasingly repulsive molecule-molecule interaction.

This paper is organized as follows. In Sec. II we consider the uniform system, and calculate the effective mass of a molecule and thermal depletion of the number of molecules. The transition temperature is discussed in Sec. III, first for a uniform gas and then for a trapped gas. Finally, Sec. IV contains concluding remarks.

## II. THE UNIFORM SYSTEM

We investigate the properties of a system containing equal numbers $N$ of two species of fermion, labelled by a pseudospin index $\sigma = \pm 1$, that can form a diatomic molecular bound state in the limit when the system consists mainly of molecules, with a small admixture of atoms. We shall assume that the two species of fermion have the same mass $m$. In the spirit of Landau, we write the effective low-energy Hamiltonian for the system as

$$\begin{aligned} H &= \sum_{\mathbf{p}} \left( -\epsilon_{\rm b} + \frac{p^2}{4m} \right) \hat{b}^\dagger_{\mathbf{p}} \hat{b}_{\mathbf{p}} + \sum_{\mathbf{q}\sigma} \frac{q^2}{2m} \hat{a}^\dagger_{\mathbf{q}\sigma} \hat{a}_{\mathbf{q}\sigma} \\ &+ \frac{\pi\hbar^2 a_{\rm mm}}{mV} \sum_{\mathbf{p}\mathbf{p}'\mathbf{q}} \hat{b}^\dagger_{\mathbf{p}} \hat{b}^\dagger_{\mathbf{p}'} \hat{b}_{\mathbf{p}'+\mathbf{q}} \hat{b}_{\mathbf{p}-\mathbf{q}} \\ &+ \frac{6\pi\hbar^2 a_{\rm am}}{mV} \sum_{\mathbf{p}\mathbf{p}'\mathbf{q}\sigma} \hat{a}^\dagger_{\mathbf{p}\sigma} \hat{b}^\dagger_{\mathbf{p}'} \hat{b}_{\mathbf{p}'+\mathbf{q}} \hat{a}_{\mathbf{p}-\mathbf{q}\sigma} \\ &+ \frac{4\pi\hbar^2 a_{\rm aa}}{mV} \sum_{\mathbf{p}\mathbf{p}'} \hat{a}^\dagger_{\mathbf{p}\uparrow} \hat{a}^\dagger_{\mathbf{p}'\downarrow} \hat{a}_{\mathbf{p}'+\mathbf{q}\downarrow} \hat{a}_{\mathbf{p}-\mathbf{q}\uparrow} \\ &+ \frac{g}{V^{1/2}} \sum_{\mathbf{p}\mathbf{q}} \left( \hat{b}^\dagger_{\mathbf{p}} \hat{a}_{\mathbf{q}+\mathbf{p}/2\uparrow} \hat{a}_{-\mathbf{q}+\mathbf{p}/2\downarrow} + \text{h.c.} \right) \end{aligned} \quad (1)$$

the operators $\hat{a}^\dagger$, $\hat{a}$ $\hat{b}^\dagger$, $\hat{b}$ create and destroy atoms and molecules, respectively. Here $V$ is the volume of the system, $g$ is the matrix element for decay of a molecule into two atoms and $a_{\rm ij}$ is the scattering length between a particle i and a particle j, and 'a' stands for an atom and 'm' for a molecule. The quantity $a_{\rm aa}$ is the background scattering length for atom-atom scattering due to nonresonant processes. In the case of strong coupling between the molecule and the atoms, e. g. for a broad Feshbach resonance, and in the limit of a deeply bound molecular state it has been shown that [14, 15]

$$a_{\rm ma} \approx 1.2 a_{\rm aa}, \qquad a_{\rm mm} \approx 0.6 a_{\rm aa}. \quad (2)$$

We begin by considering a uniform gas, and we first calculate the molecule spectrum. The leading contributions to the energy of a molecule are due to the molecule-molecule interactions, which give a shift $2\pi\hbar^2 n_{\rm m} a_{\rm mm}/m$ to the self energy of a molecule in the mean field of the other molecules, and a contribution one half of this to the average energy per molecule. Here $n_{\rm m}$ is the number density of molecules. Atom-molecule interactions contribute $6\pi\hbar^2 n_{\rm a} a_{\rm am}/m$ to the molecule self energy from the scattering of atoms by molecules, and from dissociation of molecules into atoms an amount

$$\begin{aligned} \delta\epsilon_{\mathbf{p}} &= g^2 \int \frac{d^3q}{(2\pi\hbar)^3} \frac{n_{\mathbf{p}/2+\mathbf{q}} + n_{\mathbf{p}/2-\mathbf{q}}}{\epsilon_{\rm b} + q^2/m} \\ &= 2g^2 \int \frac{d^3q}{(2\pi\hbar)^3} \frac{n_{\mathbf{q}}}{\epsilon_{\rm b} + (\mathbf{q}+\mathbf{p}/2)^2/m}. \end{aligned} \quad (3)$$

The term independent of the atom distribution function $n_{\mathbf{q}}$ is not included, since this is already contained in the binding energy $\epsilon_{\rm b}$ of two fermions in the absence of a medium. The contribution (3) is due to Pauli blocking of dissociation of molecules, which raises the energy of a molecule. As a consequence of Galilean invariance, in the absence of a medium, the effective mass of a molecule remains equal to the bare mass. The binding energy of a molecule with momentum zero is thus reduced by an amount

$$\delta\epsilon_{\rm b} = 2g^2 \int \frac{d^3q}{(2\pi\hbar)^3} \frac{n_{\mathbf{q}}}{\epsilon_{\rm b} + q^2/m} \simeq 2g^2 \frac{n_{\rm a}}{\epsilon_{\rm b}}, \quad (4)$$

where $n_{\rm a}$ is the density of atoms of both species. In the second expression we have assumed that the molecule is deeply bound in the sense that $\epsilon_{\rm b} \gg kT$. The molecule spectrum varies over momentum scales of order $(m\epsilon_{\rm b})^{1/2}$, and therefore for the momenta of interest in the problem of Bose-Einstein condensation, which are of order $(mkT)^{1/2}$, it is sufficient to calculate only to order $p^2$. The result is

$$\epsilon_{\mathbf{p}} \simeq -\epsilon_{\rm b} + \frac{2\pi\hbar^2 n_{\rm m} a_{\rm mm}}{m} + \frac{6\pi\hbar^2 n_{\rm a} a_{\rm am}}{m} + 2g^2 \frac{n_{\rm a}}{\epsilon_{\rm b}} + \frac{p^2}{2M^*}, \quad (5)$$

where the effective mass of a molecule is increased by an amount given by

$$\frac{1}{M^*} = \frac{1}{2m} \left( 1 - 2g^2 \frac{n_{\rm a}}{\epsilon_{\rm b}^2} \right). \quad (6)$$

We now turn to the transition temperature of the gas.

## III. TRANSITION TEMPERATURE

### A. Uniform system

For a uniform gas of elementary bosons, the transition temperature is unaffected by the Hartree mean-field energy, since this gives a shift to the energy of a boson and to the chemical potential which are independent of the momentum of the particle. However, it has been demonstrated that, due to critical fluctuations, the transition temperature is increased, by an amount which is given for small $n_{\rm m}^{1/3} a_{\rm mm}$ by [16, 17]

$$\frac{\delta T_{\rm c}}{T_{\rm c}} = b n_{\rm m}^{1/3} a_{\rm mm}, \quad (7)$$

where $b$ is a positive coefficient, which has been estimated to be approximately 1.3 [18, 19, 20]. This effect will tend to be counteracted by the increase of the effective mass and the reduction of the density of molecules due to dissociation, both of which tend to decrease the transition temperature, since for an ideal Bose gas, $T_{\rm c} \sim \hbar^2 n_{\rm m}^{2/3}/2M^*$. The number density of molecules is given by

$$n_{\rm m} = \frac{N}{V} - \frac{n_{\rm a}}{2}. \quad (8)$$

The two latter effects give changes in the transition temperature which are proportional to $n_{\rm a}/n_{\rm m} \propto e^{-\epsilon_{\rm b}/kT_{\rm c}}$. Thus for a deeply bound molecule, the effects of critical fluctuations dominate, and the transition temperature initially increases away from the BEC limit. Since in the BCS limit the transition temperature tends to zero, we conclude that the transition temperature must have a local maximum, provided that the transition temperature is a continuous function of the scattering length.

### B. Trapped cloud

We now turn to the case of a cloud in a harmonic trap, and we shall assume that the trapping potentials for the two species of fermion are the same, and equal to one half of the trapping potential for a molecule. Previously, the transition temperature for a trapped gas of bosons has been calculated with allowance for the nonzero spacing of the single-particle levels in the oscillator potential and for the distortion of the density profile by the interaction and the result is [21]

$$\frac{\delta T_{\rm c}}{T_{\rm c}} \approx -0.73\frac{\omega_{\rm m}}{\bar{\omega}}N^{-1/3} - 1.33\frac{a_{\rm mm}}{\bar{a}}N^{1/6}, \qquad (9)$$

where $\omega_{\rm m}$ is the algebraic mean of the trap frequencies for the three principal axes of the trap, $\bar{\omega}$ is their harmonic mean and $\bar{a} = (\hbar/m\bar{\omega})^{1/2}$ is the mean harmonic oscillator length.

To take account of critical fluctuations, we argue that provided the typical interaction energy between molecules, $2\pi\hbar^2 n_{\rm m} a_{\rm mm}/m$ is large compared with the oscillator quantum of energy but small compared with $kT_{\rm c}$, it should be a good approximation to calculate the change in $T_{\rm c}$ in a local density approximation, in which the central density of the cloud is inserted in Eq. (7). The central density $n_{\rm m}(0)$ at $T_{\rm c}$ is given by

$$n_{\rm m}(0) = \zeta(3/2)\left(\frac{MkT_{\rm c}}{2\pi\hbar^2}\right)^{3/2}, \qquad (10)$$

and since $kT_{\rm c} = [N/\zeta(3)]^{1/3}\hbar\bar{\omega}$, it follows that the contribution to the change in $T_{\rm c}$ due to critical fluctuations is

$$\frac{\delta T_{\rm c}}{T_{\rm c}} \approx \frac{1.3}{(2\pi)^{1/2}}\frac{[\zeta(3/2)]^{1/3}}{[\zeta(3)]^{1/6}}N^{1/6}\frac{a_{\rm mm}}{\bar{a}}. \qquad (11)$$

Calculations indicate that critical fluctuations are suppressed in inhomogeneous systems [22], so we regard this estimate as an upper limit to the increase of $T_{\rm c}$. Adding this to the earlier result (9) without fluctuations, we find for the total change in $T_{\rm c}$

$$\frac{\delta T_{\rm c}}{T_{\rm c}} \approx -0.73\frac{\omega_{\rm m}}{\bar{\omega}}N^{-1/3} - 0.64\frac{a_{\rm mm}}{\bar{a}}N^{1/6}. \qquad (12)$$

Thus, in contrast to the uniform case, the change in $T_{\rm c}$ for small $a_{\rm mm}$ is *negative*, since the effect of critical fluctuations is overwhelmed by the reduction of the central density.

The discussion we have given above applies to broad Feshbach resonances, for which the energy dependence of the atomic interactions may be neglected. For narrow Feshbach resonances, critical fluctuations are suppressed because the magnitude of the contribution from processes in which the argument of the interaction contains a frequency which is to be summed over will be reduced because of the strong reduction of the interaction away from resonance, as discussed in Ref. [23].

## IV. CONCLUSION

In this paper we have identified a number of effects that produce changes in the transition temperature away from the BEC limit. Two of these are due to thermal dissociation of molecules, and these lead to a decrease in $T_{\rm c}$. However, for a uniform gas, these effects are overwhelmed by a rise in $T_{\rm c}$ due to the increasingly repulsive molecule-molecule interaction. We therefore conclude, quite generally, that $T_{\rm c}$ must display a global maximum between the BEC and BCS limits for a broad Feshbach resonance. For trapped gases, we have argued that $T_{\rm c}$ will initially decrease away from the BEC limit. Thus, on the basis of the arguments given here, there need not be a maximum in $T_{\rm c}$ but it cannot be excluded. Likewise, for a narrow Feshbach resonance, critical fluctuations are suppressed, and consequently $T_{\rm c}$ is expected to decrease away from the BEC limit.

The framework we have described in this paper could be a useful tool for analysis of detailed crossover calculations, since it points to a number of quantities that could be calculated in order to test our fundamental understanding.

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[1] D. M. Eagles, *Phys. Rev.* **186**, 456 (1969).
[2] A. J. Leggett, *J. Phys. (Paris) Colloq.* **41**, C7-19 (1980).
[3] P. Nozières and S. Schmitt-Rink, *J. Low Temp. Phys.* **59**, 195 (1985).
[4] M. Drechsler and W. Zwerger, *Ann. Phys.* **1**, 15 (1992).
[5] C. A. R. Sá de Melo, M. Randeria and J. R. Engelbrecht, *Phys. Rev. Lett.* **71**, 3202 (1993).
[6] R. Haussmann, *Phys. Rev. B*, **49**, 12975 (1994).
[7] R. Haussmann, W. Rantner, S. Cerrito, and W. Zwerger, cond-mat/0608282.
[8] J. N. Milstein, S. J. J. M. F. Kokkelmans, and M. J. Holland, *Phys. Rev. A*, **66**, 043604 (2002).
[9] Y. Ohashi and A. Griffin, *Phys. Rev. Lett.* **89**, 130402 (2002).
[10] Y. Ohashi and A. Griffin, *Phys. Rev. A*, **67**, 033603 (2003).
[11] Q. Chen, J. Stajic, and K. Levin, *Phys. Rep.* **412**, 1 (2005).
[12] A. Perali, P. Pieri, and G. C. Strinati, *Phys. Rev. Lett.* **92**, 220404 (2004).
[13] G. M. Falco and H. T. C. Stoof, cond-mat/0603270.
[14] G. Skornyakov and K. A. Ter-Martirosian, Zh. Eksp. Teor. Fiz. 31, 775 (1956)[Soviet Physics JETP 4, 648 (1957)].
[15] D. S. Petrov, C. Salomon, and G. V. Shlyapnikov, *Phys. Rev. Lett.* **93**, 090404 (2004).
[16] G. Baym, J.-P. Blaizot, M. Holzmann, F. Laloë, and D. Vautherin, *Phys. Rev. Lett.* **83**, 1703 (1999).
[17] The importance of critical fluctuations in tending to increase $T_c$ has also been pointed out in Ref. [7].
[18] P. Arnold and G. Moore, *Phys. Rev. Lett.* **87**, 120401 (2001).
[19] V. A. Kashurnikov, N. V. Prokof'ev, and B. V. Svistunov, *Phys. Rev. Lett.* **87**, 120402 (2001).
[20] In the calculations of the critical fluctuations, the energy dependence of the effective interaction is neglected and consequently the result is appropriate for a broad Feshbach resonance. We shall later return to the case of a narrow resonance.
[21] S. Giorgini, L. P. Pitaevskii, and S. Stringari, *Phys. Rev. A* **54**, 4633 (1996).
[22] O. Zobay, G. Metikas, and H. Kleinert, *Phys. Rev. A* **71**, 043614 (2005).
[23] A. Schwenk and C. J. Pethick, *Phys. Rev. Lett.* **95**, 160401 (2005).